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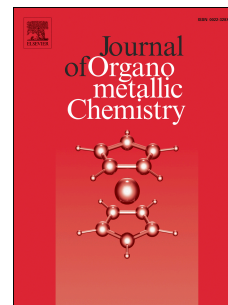
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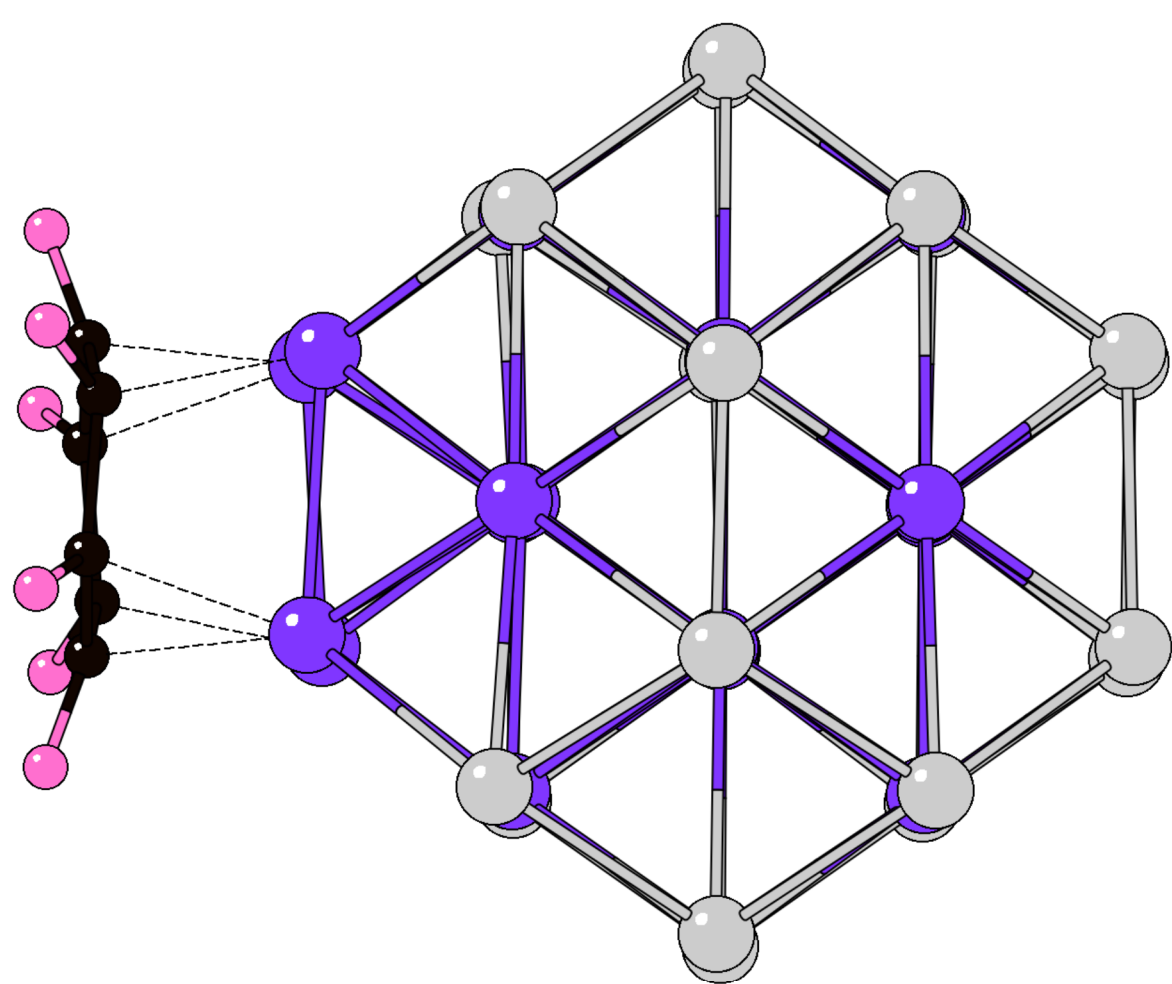
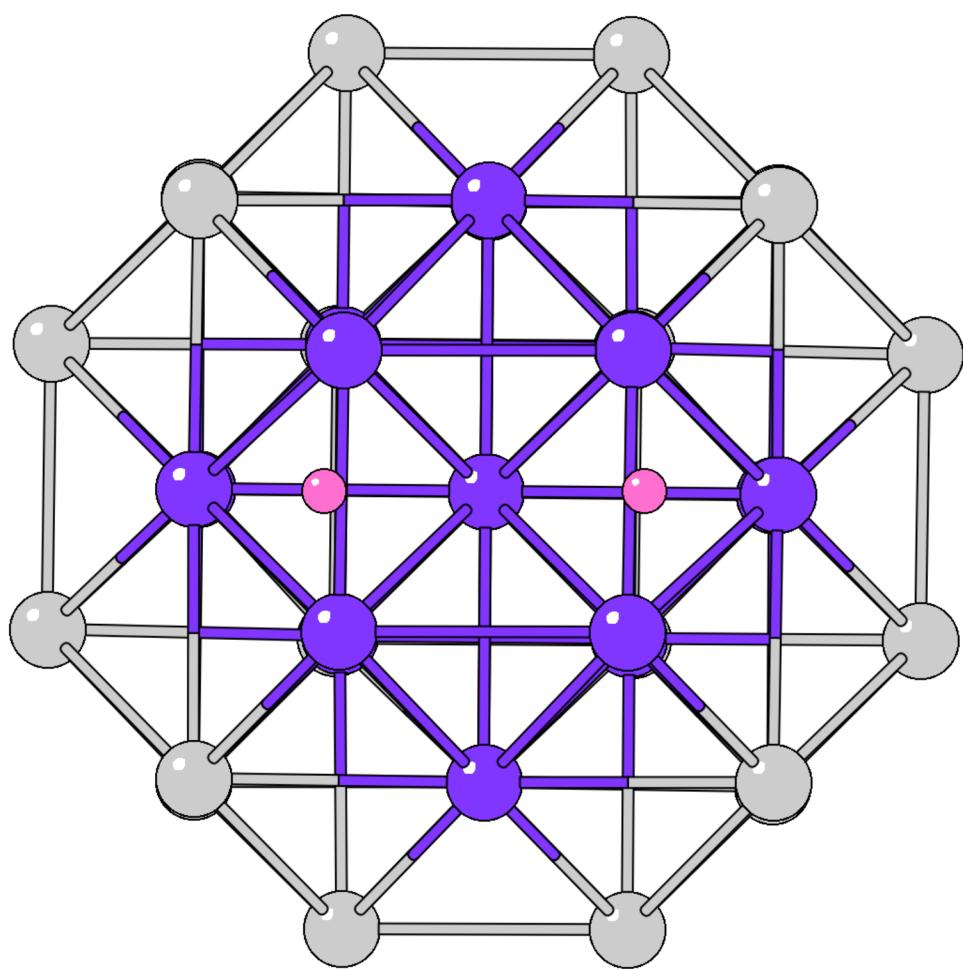
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# Computational Study of the Adsorption of Benzene and Hydrogen on Palladium-Iridium Nanoalloys

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## Abstract

The preferred chemisorption sites on a variety of palladium-iridium nanoalloys are determined for benzene and hydrogen molecules. Available sites on the surface of the nanoalloys are explored using a random-search method, directly at the density functional level of theory. These searches successfully reveal the site preference for benzene and significant nanosize effects in the chemisorption of hydrogen. It is hoped that through the study of the chemisorption properties of Pd-Ir nanoalloys, complex catalytic processes, such as tetralin hydroconversion and the preferential oxidation of CO, can be better understood.

**Keywords:** DFT, Palladium, Iridium, Nanoalloy, Catalysis, Benzene, Hydrogen

## 1. Introduction

Nanoalloys (NAs) are a class of nanomaterials composed of two or more metallic elements. These include nanoparticles (NPs), 2D-like structures, such as nanogrids and sheets, and 1D-like structures, such as nanowires and nanotubes.[1] The combination of metals in a NP results in properties which are dependent not only on size and shape,[2] but also on the composition and chemical ordering.[3] The presence of two or more metals introduces homotops, isomers differing in only the ordering of elements.[4]

Palladium-iridium is a strongly demixing alloy system[5, 6, 7]. This is reflected in the structural characteristics of the corresponding nanoalloys.[8, 9] Pd-Ir nanoalloys have been investigated previously for application in a number of catalytic processes,[10, 11, 12, 13, 14, 15, 16] including tetralin hydroconversion through selective ring opening,[14] a process which is key to understanding how to reduce particulate emissions from diesel fuel. Here it was hoped the catalytic properties of each metal would be combined in the nanoalloy catalyst. Ir has been shown to be active in C-C bond hydrogenolysis.[17] Pd shows improved hydrogen activation and thioresistance over other noble metal catalysts. Through alloying, depending on the relative proportions of metals, increased activity and selectivity can be obtained.

Understanding the role of hydrogen in tetralin hydroconversion and other reactions, such as the preferential oxidation of CO (PROX), is vital.[15, 16] Bulk Pd is the only metal at ambient temperature and hydrogen pressure to form a hydride.[18, 19] Nanosize effects on the Pd-H system have been widely studied.[19, 20] Nanosize Pd exhibits an increased hydrogen

absorption rate and decreased adsorption capacity.[21, 22] Recently, the interaction of hydrogen with Pd, Ir and Pd-Ir was probed, with nanosized-induced hydrogen absorption being reported for Ir.[23, 16] The sorption (adsorption+absorption) capacity of Pd-Ir nanoalloys was found to be strongly reduced compared with the pure NPs.[16] Furthermore, the addition of Ir to Pd inhibits the formation of Pd hydride. This is thought to be beneficial to the activity of Pd-Ir as a catalyst since the hydride is unselective in PROX.

Theoretical studies of the interaction of molecular hydrogen with nanoalloys are limited. Pd, Pt and Pd-Pt nanoparticles (NPs) have been investigated previously using density functional theory (DFT).[24, 25] Kozlov and co-workers investigated the differences between the adsorption and absorption of hydrogen atoms on Pd and Pt NPs.[25] The work was found to be in agreement with previous studies suggesting that hydrogen dissociatively adsorbs in the subsurface of Pd.

A study of the interactions between benzene and hydrogen molecules with a range of Pd-Ir nanoalloys is presented here. The nanoalloy structures are truncated octahedra (TOs), whose chemical ordering has been predicted using the Free-Energy Concentration Expansion Method with coordination-dependent bond energy variations (FCM/CBEV).[8] The FCM/CBEV lowest energy TO homotops for Pd<sub>4</sub>Ir<sub>34</sub>, Pd<sub>8</sub>Ir<sub>30</sub> and Pd<sub>20</sub>Ir<sub>18</sub>, are studied alongside monometallic Pd<sub>38</sub> and Ir<sub>38</sub>. Although for 38-atoms the TO is almost certainly not the global minimum, it is representative of the TO structures seen for larger Pd-Ir particles.[14]

## 2. Methodology

### 2.1. DFT

Gamma-point, spin-polarised DFT calculations were performed using VASP.[26, 27, 28, 29, 30] Projected-augmented

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wave pseudopotentials were used with the PBEsol exchange correlation functional.[31, 32] A plane-wave basis set with a cut-off of 400 eV was used. Methfessel-Paxton smearing, with a sigma value of 0.01 eV, was used to improve metallic convergence.[33]

## 2.2. Search Method

To determine the site preferences for both benzene and hydrogen, a DFT-based random search method was utilised, analogous to the *ab initio* random search (AIRS) approach of Pickard et al.[34] To begin a search an initial configuration of the ligand-cluster system was generated by placing a single ligand molecule tangential to a locally minimised cluster. The random search then consisted of a fixed numbers of steps. A step in the search combined a random rotation move with a local minimisation at the DFT level.

The random rotation was performed on the cluster whilst keeping the position of the ligand molecule fixed. After each selective rotation a local minimisation was performed using VASP. These calculations were performed at 0 K and, therefore, no atom diffusion occurred. This methodology was able to sample comprehensively the available adsorption sites on the surface of the cluster.

## 2.3. Energetics

The adsorption energy,  $E_{\text{ads}}$  for each cluster was defined as the difference between the energy of the cluster with adsorbate,  $E_{\text{cluster+ligand}}$ , and the sum of the energies of the bare cluster,  $E_{\text{cluster}}$  and gas-phase ligand,  $E_{\text{ligand}}$ , as shown in equation 1.

$$E_{\text{ads}} = E_{\text{cluster+ligand}} - (E_{\text{cluster}} + E_{\text{ligand}}) \quad (1)$$

## 3. Results

### 3.1. Benzene

The Pd-Ir FCEM/CBEV TO homotop structures used in the searches are shown in Figure 1. Each clearly shows Pd segregating to the surface of the cluster, giving a variety of mono- and bimetallic adsorption sites. The segregation of Pd is favoured by the lower surface energy of Pd compared to Ir.

For each composition, local minimisations were carried out on 50 random chemisorption sites. The adsorption energies of the most favourable sites are given in Table 1. The lowest energy structures are given in Figure 2. Benzene was found to chemisorb most favourably to Ir and Ir-rich clusters, with  $E_{\text{ads}}$  of around -4.5 eV. This interaction diminishes as the proportion of Pd is increased.

The graph in Figure 3 shows the ordered chemisorption energies from each random search. The plot gives an indication as to how many inequivalent sites have been explored for each composition. Several steps taken for Pd<sub>4</sub>Ir<sub>34</sub> and Pd<sub>8</sub>Ir<sub>30</sub> produce non-interacting structures, shown by  $E_{\text{ads}}$  values around 0 eV. In some cases energetically equivalent minima are sampled multiple times producing steps on the plots. This is shown by the Ir<sub>38</sub> plot, which exhibits eight clearly inequivalent steps. Many of the smaller differences seen for the other compositions

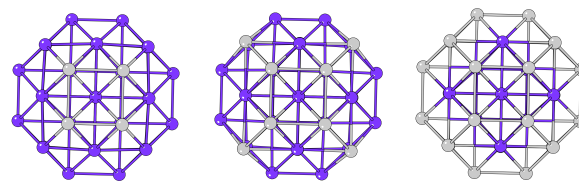


Figure 1: Top views of the FCEM/CBEV lowest energy homotop structures for Pd<sub>4</sub>Ir<sub>34</sub>, Pd<sub>8</sub>Ir<sub>30</sub> and Pd<sub>20</sub>Ir<sub>18</sub> shown from left to right. Ir and Pd are shown in gold and silver, respectively.

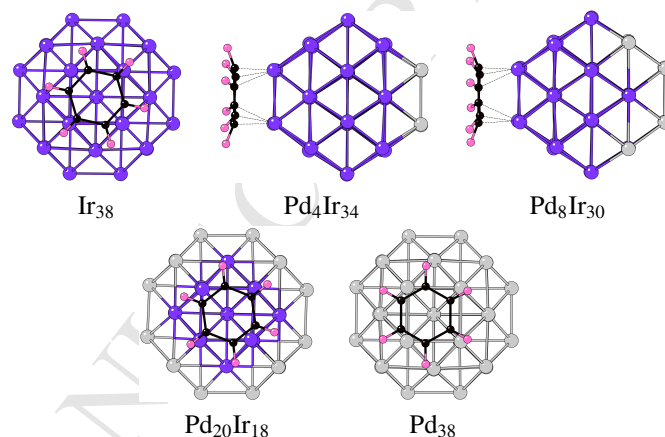


Figure 2: Lowest energy benzene chemisorption site for each composition. Pd, Ir, C and H are shown in silver, gold, black and pink, respectively.

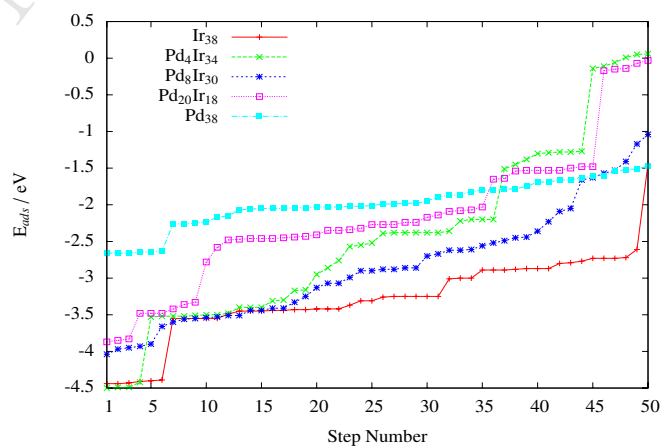


Figure 3: Adsorption energies for the 50 random steps taken for each nanoalloy composition in the presence of benzenes. Energies are ordered from lowest to highest.

may arise from the greater orientational flexibility of the benzene molecule.

The lowest energy site found for Pd<sub>38</sub> and Ir<sub>38</sub> was the (100) face of the TO. For Pd<sub>4</sub>Ir<sub>34</sub> and Pd<sub>20</sub>Ir<sub>18</sub> the lowest energy site was the Ir (100) face of the cluster. The lowest energy site found on Pd<sub>8</sub>Ir<sub>30</sub> was a bimetallic (100) face but on closer inspection, the monometallic Ir (100) face had not been explored by the random search. A local minimisation was carried out with ben-



zene placed at the (100) site. This was found to be the new lowest energy site.

These results compare favourably with those from previous studies of benzene adsorption on bulk metal surfaces. The adsorption energies reported for the Ir(100) and Pd(100) surfaces are -2.88 eV and -2.03 eV, respectively.[35, 36] These are considerably larger (in absolute values) than the corresponding (111) values and explain the preference for the (100) site on the TO.[37] The  $E_{\text{ads}}$  reported for the NA clusters are considerably larger than those values reported for the bulk metal surfaces. This suggests a significant nanosize effect, especially in case of the pure Ir and Ir-rich clusters.

After adsorption, significant strain can be seen in the benzene molecule. Figure 4 shows benzene chemisorbed onto  $\text{Pd}_{20}\text{Ir}_{18}$ . The benzene structure is distorted with C-H bonds clearly bent away from the cluster. The amount of strain a NA can introduce into a benzene molecule could be related to its catalytic activity in the ring opening of cyclic hydrocarbons.

Table 1: The average C-C bond lengths,  $R_{\text{C-C}}$ , and adsorption energies,  $E_{\text{ads}}$  for benzene on the Pd, Ir and Pd-Ir clusters.

Composition	$R_{\text{C-C}} / \text{\AA}$	$E_{\text{ads}} / \text{eV}$
$\text{Ir}_{38}$	1.46	-4.44
$\text{Pd}_4\text{Ir}_{34}$	1.46	-4.50
$\text{Pd}_8\text{Ir}_{30}$	1.46	-4.44
$\text{Pd}_{20}\text{Ir}_{18}$	1.46	-3.87
$\text{Pd}_{38}$	1.41	-2.66

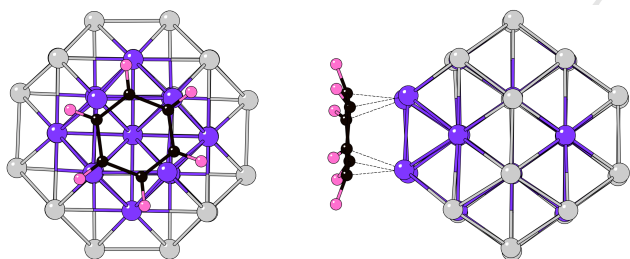


Figure 4: Top and side views of the lowest energy chemisorption site for benzene on  $\text{Pd}_{20}\text{Ir}_{18}$ .

### 3.2. Hydrogen

For each composition, local minimisations were carried out on 50 random chemisorption sites. The chemisorption energies and structures of the most favourable sites are given in Table 2 and figure 5.

For  $\text{Pd}_{38}$  molecular hydrogen is found to chemisorb non-dissociatively at a large number of sites on the cluster. This differs from  $\text{Ir}_{38}$  where for each site explored hydrogen is found to dissociate upon chemisorption. On the mixed clusters, the number of dissociated hydrogen molecules was found to increase as the Ir content of the cluster increased (Table 2).

The lowest energy site for each composition is found to be one in which the hydrogen molecule has dissociated. For the

Table 2: The total number of dissociated hydrogen molecules,  $N_{\text{diss}}$ , and lowest adsorption energy,  $E_{\text{ads}}$ , from 50 random search steps for hydrogen on the Pd, Ir and Pd-Ir clusters.

Composition	$N_{\text{diss}}$	$E_{\text{ads}} / \text{eV}$
$\text{Ir}_{38}$	50	-1.98
$\text{Pd}_4\text{Ir}_{34}$	50	-1.94
$\text{Pd}_8\text{Ir}_{30}$	44	-1.95
$\text{Pd}_{20}\text{Ir}_{18}$	42	-1.64
$\text{Pd}_{38}$	28	-1.46

Ir and Pd-Ir clusters each hydrogen atom is chemisorbed to an edge site of a (100) face. For  $\text{Pd}_{38}$  each hydrogen is found to chemisorb to a *fcc* site on a (111) face. These results correlate well with those from a previous DFT study of the bulk metal surfaces.[38] Hydrogen was found to favour the bridge sites on the Ir(100) surface, equivalent to the edge sites on the cluster. On Pd the *fcc* sites on the (111) surface were preferred, equivalent to *fcc* sites on the (111) face of the TO.

The difference in  $E_{\text{ads}}$  for a hydrogen atom on the Ir(100) bridge and Ir(111) *fcc* sites was reported as 0.3 eV. This correlates with the preference for hydrogen to chemisorb to the (100) edge sites of the Ir and Ir-rich clusters. Pd shows the opposite order with a difference in  $E_{\text{ads}}$  for the Pd(100) four-fold and Pd(111) *fcc* sites of -0.7 eV. This again correlates with the hydrogen's preference for the (111) *fcc* sites on the Pd TO.

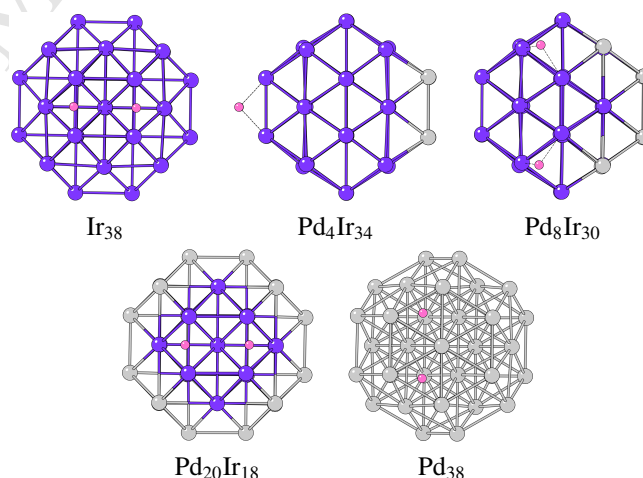


Figure 5: Lowest energy hydrogen chemisorption site for all compositions, each with dissociated hydrogen shown in pink.

## 4. Conclusions

In real world catalytic processes Pd-Ir NAs are exposed to multiple reactants. Understanding the chemisorption properties of Pd, Ir and Pd-Ir clusters can aid in the full description of their catalytic properties in these complex environments. It is thought that the combination of Pd and Ir promotes PROX catalytic performance by preventing poisoning through hydrogen sorption.

In this study, significant nanosize effects are seen in the adsorption of hydrogen. Hydrogen is found to dissociate and chemisorb most strongly on pure Ir and Ir-rich clusters. On Pd and Pd-rich clusters hydrogen is often found to chemisorb associatively. The effect of composition on chemisorption is more pronounced for hydrogen than for benzene, with a greater variety of energies and differing site preferences for pure hydrogen adsorption on Pd and Ir.

The strongly segregating Pd-Ir clusters display a wide variety of sites on their surfaces. In tetralin hydroconversion in the presence of H<sub>2</sub>S, it could be the case that iridium provides the strongest chemisorption sites for the aromatic ring, whilst the presence of Pd helps to prevent the poisoning of the catalyst because of its weaker interaction with sulphur.[39]

Future studies will include the development of automatic search techniques for the global optimisation of NAs in the presence of ligands. Theoretical work could be extended to the benzene+hydrogen reaction. It is hoped that this and future work can be used to aid in the explanation of experimental work on the Pd-Ir system.

The nanosize effects seen in Pd and Ir clusters will be further investigated. Studies will include calculating the energy barriers to hydrogen dissociation and investigating the adsorption properties of the bulk materials and clusters of a greater variety of size, shape and composition.

## 5. Acknowledgements

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- A random search at the density functional level of theory is used to determine the site preference for the adsorption of benzene and hydrogen on a variety of Pd-Ir nanoalloys.
- Significant nanosize effects are seen in the chemisorption of hydrogen.
- The site preferences for both benzene and hydrogen are found to correlate with their preference on the analogous bulk surfaces.